

# Synthesis, Structure and Photoelectric Property of a 3D Supramolecular Zinc Coordination Polymer

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**ABSTRACT** Using a rigid azo ligand 4-[(8-hydroxy-5-quinoliny)azo]-benzoic acid ( $H_2L$ ), a new supramolecular compound  $[Zn(L)(H_2O)_2]_n$  (**1**) has been solvothermally synthesized and structurally characterized by X-ray single-crystal diffraction, infrared spectrum, elemental analysis, power X-ray diffraction and thermal analysis. Compound **1** crystallizes in monoclinic, space group  $C2/c$  with  $a = 30.372(8)$ ,  $b = 11.415(3)$ ,  $c = 9.248(3)$  Å,  $\beta = 106.94(3)^\circ$ ;  $V = 3067.20(15)$  Å<sup>3</sup>,  $C_{16}H_{13}N_3O_5Zn$ ,  $M_r = 392.66$ ,  $Z = 8$ ,  $D_c = 1.701$  Mg/m<sup>3</sup>;  $F(000) = 1600$ ,  $\mu = 1.636$  mm<sup>-1</sup>, reflections collected: 7290, reflections unique: 2735,  $R_{int} = 0.0282$ ,  $R = 0.0351$ ,  $wR$  (all data) = 0.0919,  $GOOF$  on  $F^2 = 1.036$ . Compound **1** exhibits a one-dimensional (1D) zig-zag chain structure connected into a three-dimensional (3D) supramolecular network through hydrogen bonding interactions. Fluorescent property and electrochemical property were detected on compound **1**.

**Keywords:** coordination polymer; co-sensitization; solar cell; fluorescent property; electrochemical property; DOI: 10.14102/j.cnki.0254-5861.2011-1755

## 1 INTRODUCTION

Over the past decade, many people fascinated supramolecular coordination polymer materials constructed by organic bridging ligands and transition metal ions because they possessed various architectures and multiple applications in molecular recognition, sensors, photology and electrochemistry<sup>[1-5]</sup>. During the process of constructing these supramolecular coordination polymer materials, a valid selection or design of multifunctional organic ligands is crucial to conceivable functions<sup>[6-9]</sup>. As one of the azo organic ligands, 4-[(8-hydroxy-5-quinoliny)azo]-benzenesulfonic acid may be a desired ligand due to its structural

characteristic<sup>[10-14]</sup>: (i) It reveals diversiform coordination abilities because it has multiple coordination sites. (ii) Owing to simultaneous possessing the O and N atoms, it could take on the acceptors or donors of hydrogen bonding to assemble various supramolecular structures. (iii) Quinoline ring has a strong chelating ability to combine with metal ions attributing to the ortho position between hydroxyl and N atom. On the other hand, metal organic coordination polymers with optical performance have been tentatively used in the field of dye-sensitized solar cells (DSSCs) as spectral sensitizers in recent years<sup>[15]</sup>. Grätzel groups successfully co-sensitized squarylium cyanine dye and bithiophene dye based on nanocrystalline TiO<sub>2</sub> films. Fortunately, the whole photoelectric conversion efficiency can reach 7.43%. This value reported for co-sensitized DSSC with metal organic coordination polymers is the highest so far<sup>[16]</sup>. Based on the above, H<sub>2</sub>L may be a commendable ligand to construct supramolecular coordination polymer materials, which can own multifarious structures, excellent fluorescent performance and favorable electrochemical property.

## 2 EXPERIMENTAL

### 2.1 Materials and instruments

IR (KBr pellets) spectra were taken on a Nicolet Impact 410 FT-IR spectrometer in the 4000~400 cm<sup>-1</sup> range and elemental analyses for C, H and N were performed on a Perkin-Elmer 2400 Elemental Analyzer. PXRD were performed on a Siemens D5005 diffractometer, using Cu-K $\alpha$  ( $\lambda$  = 0.15418 nm) with a graphite monochromator. Thermal studies were recorded by thermogravimetric analyses (TGA) on a Perkin-Elmer TGA 7 thermogravimetric analyzer with a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub>. The fluorescence property was detected by LS55 luminescence spectrometer. Electrochemical impedance was measured by chi660d electrochemical work-station with three-electrode system in the dark. Frequency range was 0.05~105 Hz, and the applied potential was generally between 0~0.700 V. Under AM 1.5 illumination intensity (100 mW cm<sup>-2</sup>) by using a solar simulator, the photocurrent-photovoltage (*J*-*V*) curve of the sealed cells was measured. The fill factor (*FF*) and the photoelectric conversion efficiency ( $\eta$ ) are defined as  $FF = (J_{\max} \times V_{\max}) / (J_{\text{sc}} \times V_{\text{oc}})$  and  $\eta = (FF \times J_{\text{sc}} \times V_{\text{oc}}) / P_{\text{in}}$ , respectively ( $J_{\max}$  and  $V_{\max}$  are the photocurrent density and photovoltage for maximum power output, respectively.  $J_{\text{sc}}$  and  $V_{\text{oc}}$  are the shortcircuit photocurrent density and open-circuit photovoltage, respectively.  $P_{\text{in}}$  is the power of incident light).

### 2.2 Synthesis of [Zn(L)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>

A mixture of ZnCl<sub>2</sub> (30 mg, 0.22 mmol), H<sub>2</sub>L (5 mg, 0.015 mmol), ethanol (10 mL), H<sub>2</sub>O (2 mL) and

dimethyl formamide (DMF, 2 mL) was stirred at 25 °C till getting a clarified red solution. After 2 h reaction, the pH value was adjusted with 2 mol/L NaOH to 5.0, and the mixture was finally sealed in a 25 mL Teflon-lined stainless-steel vessel and heated at 100 °C for 3 days. Then, it was cooled to 25 °C for 18 h with a programmed cooling course. Red block crystals were filtered and washed with deionized water, finally dried in air. Yields based on Zn are 50%. Elemental anal. calcd. (%) for  $C_{16}H_{13}N_3O_5Zn$  (392.66): C, 48.89; H, 3.31; N, 10.69%. Found: C, 47.54; H, 3.03; N, 10.12%. IR (KBr pellet,  $\nu/\text{cm}^{-1}$ , Fig. S1): 3448 (s), 1602 (w), 1540 (m), 1502 (s), 1516 (s), 1466 (s), 1409 (s), 1398 (s), 1386 (s), 1253 (m), 1189 (s), 1131 (s), 1035 (m), 852 (w).

### 2.3 Structure determination

A red single crystal with dimensions of 0.30 mm  $\times$  0.10 mm  $\times$  0.10 mm was measured on a Bruker Apex II CCD area-detector diffractometer (MoK $\alpha$ , 0.71070 Å) at 293 K. A total of 7290 reflections were collected by a  $\varphi$ - $\omega$  scan mode at room temperature including 2735 independent ones with  $R_{\text{int}} = 0.0282$ , of which 2319 were observed with  $I > 2\sigma(I)$ . Using the SADABS program, an empirical absorption correction was used to the measured data. The structure of compound **1** was solved by direct methods (SHELXS-97, Sheldrick, 1997) and refined by full-matrix least-squares techniques on  $F^2$ <sup>[17]</sup>. All non-hydrogen atoms were refined anisotropically. H atoms were placed geometrically by the OLEX 2 program<sup>[18]</sup>. The  $R = 0.0351$  and  $wR = 0.0919$  ( $w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 3.2819P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ ).  $(\Delta/\sigma)_{\text{max}} = 0.002$ ,  $S = 1.036$ ,  $(\Delta\rho)_{\text{max}} = 0.581$  and  $(\Delta\rho)_{\text{min}} = -0.443$  e/Å<sup>3</sup>. Selected bond lengths and bond angles are given in Table 1, and the hydrogen bond distances and bond angles in Table 2.

### 2.4 Fabrication of DSSCs

TiO<sub>2</sub> film was 0.25 cm<sup>2</sup>. The film electrodes were soaked in compound **1** solution for 3 h at room temperature (solvent is absolute ethanol, the concentration is  $5 \times 10^{-4}$  M). And then the film electrodes were soaked in N719 solution for 20 h at room temperature (The solvent mixture is acetonitrile and absolute ethanol in volume ratio of 1:1, with the concentration to be  $5 \times 10^{-4}$  M). Finally, the co-sensitized films were dried in air. A thermally platinized conducting glass (5 mM H<sub>2</sub>PtCl<sub>6</sub> in dry isopropanol, heated at 400 °C for 10 min) can act as the counter electrodes. 0.5 M LiI, 0.05 M I<sub>2</sub>, and 0.1 M 4-tertbutylpyridine in 1:1 (volume ration) acetonitrile-propylene carbonate can compose the electrolyte.

**Table 1. Selected Bond Lengths (Å) and Bond Angles (°)**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)–O(1) <sup>i</sup>	2.074(2)	Zn(1)–O(4)	2.083(2)	Zn(1)–O(5)	2.024(2)

Zn(1)–O(3)	1.988(2)	Zn(1)–N(3) <sup>i</sup>	2.096(2)	N(1)–N(2)	1.258(3)
Angle	(°)	Angle	(°)	Angle	(°)
O(3)–Zn(1)–O(1) <sup>i</sup>	92.13(8)	O(3)–Zn(1)–O(4)	93.12(9)	O(5)–Zn(1)–N(3) <sup>i</sup>	98.38(8)
O(3)–Zn(1)–O(5)	99.86(9)	O(3)–Zn(1)–N(3) <sup>i</sup>	161.24(10)	O(4)–Zn(1)–N(3) <sup>i</sup>	89.32(8)
O(5)–Zn(1)–O(1) <sup>i</sup>	101.61(8)	O(1) <sup>i</sup> –Zn(1)–N(3) <sup>i</sup>	79.91(8)	O(5)–Zn(1)–O(4)	95.89(9)
O(1) <sup>i</sup> –Zn(1)–O(4)	160.58(8)				

Symmetry transformation: i: 0.5+x, 0.5–y, 0.5+z

**Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°)**

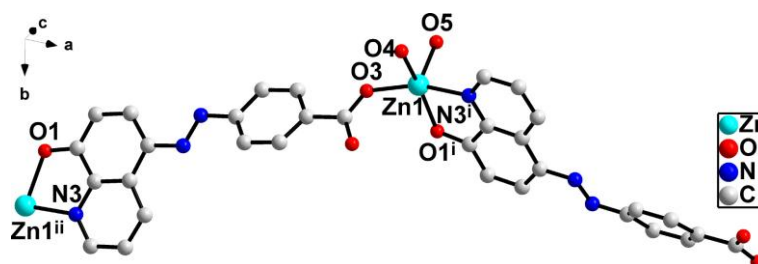
D–H...A	d(D–H)	d(H...A)	d(D...A)	∠DHA
O(4)–H(4A)...O(1) <sup>iii</sup>	0.85	1.97	2.751(3)	153
O(5)–H(5A)...O(2) <sup>iv</sup>	0.85	1.96	2.767(3)	159
O(5)–H(5B)...O(2) <sup>v</sup>	0.85	1.75	2.581(3)	164

Symmetry codes: iii: 1–x, –y, 1–z; iv: 1.5–x, –0.5+y, 1.5–z; v: x, –y, 0.5+z

### 3 RESULTS AND DISCUSSION

#### 3.1 Crystal structure

Compound **1** was synthesized by ZnCl<sub>2</sub> and H<sub>2</sub>L ligand under solvothermal conditions. Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic system, space group *C2/c*, which exhibits an infinite 1D zig-zag chain structure. As shown in Fig. 1, the asymmetrical unit of compound **1** contains one Zinc(II) atom, one L<sup>2–</sup> ligand and two coordinated water molecules. Zn1 atom is five-coordinated by four oxygen atoms (O(1)<sup>i</sup>, O(3), O(4), O(5)) and one nitrogen atom (N(3)<sup>i</sup>), forming a slightly distorted rectangular pyramidal configuration. Among them, (O(1)<sup>i</sup>, O(3), O(4), N(3)<sup>i</sup>) form a plane, and (O(5)) looks like the peak of the rectangular pyramid configuration, as shown in Fig. S2. The distances of Zn–O/N (1.988(2)~2.096(2) Å) are comparable with those found in other related Zinc(II) complexes<sup>[19]</sup>.



**Fig. 1. Coordination environments of Zn1 in compound 1**  
(Symmetry codes: i: 0.5+x, 0.5–y, 0.5+z; ii: –0.5+x, 0.5–y, –0.5+z)

In compound **1**, every L<sup>2–</sup> gives three donors for coordination, and the coordination mode of the carboxyl group exhibits a monodentate fashion, as shown in scheme S1. L<sup>2–</sup> ligand shows a  $\mu_2$ -terdentate mode, in which the 8-HQ group coordinates to one Zn(II) cation in a bidentate chelating mode, and the carboxylic acid

group adopts a monodentate fashion to coordinate with the other Zn(II) cation. As shown in Fig. 2, Zn(II) cations are linked into an infinite zig-zag chain along the *a* axis by  $L^{2-}$  ligands with an adjacent sinusoidal ruffling motif Zn  $\cdots$  Zn distance of *ca.* 29.06 Å.

In the crystal building, each zig-zag chain interacts with adjacent chains into a 3D supramolecular network by hydrogen bonds. Crystal structure reveals that the 1D zig-zag chains were connected to each other due to the O–H  $\cdots$  O interactions ( $d(O(4) \cdots O(1)^{iii}) = 2.751(3)$  Å,  $\angle O(4)–H(4A) \cdots O(1)^{iii} = 153^\circ$ ;  $d(O(5) \cdots O(2)^{iv}) = 2.767(3)$  Å,  $\angle O(5)–H(5A) \cdots O(2)^{iv} = 159^\circ$ ), forming a 2D layer structure, as shown in Fig. 3(a).  $O(5)$  acting as a hydrogen bond donor bonds to  $O(2)^v$  from the two neighboring supramolecular layers to form a 3D supramolecular network ( $d(O(5) \cdots O(2)^v) = 2.581(3)$  Å,  $\angle O(5)–H(5B) \cdots O(2)^v = 164^\circ$ ), as shown in Fig. 3(b).

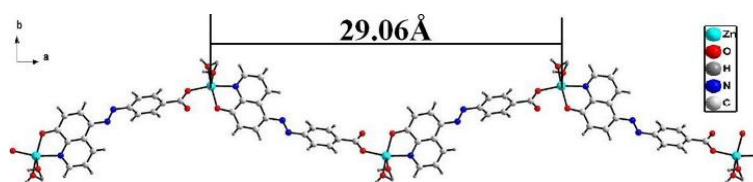


Fig. 2. 1D chain structure in compound 1

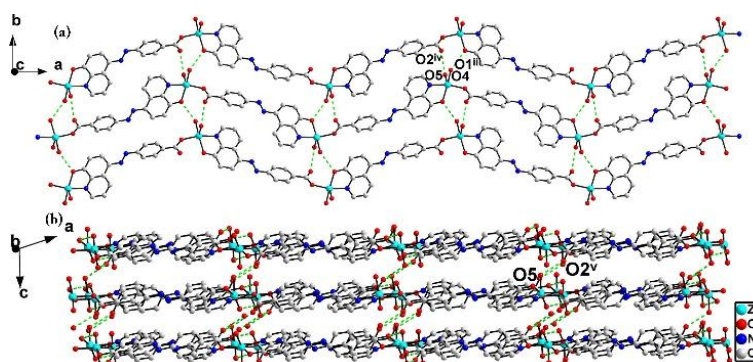


Fig. 3. (a) 1D chains are connected into a 2D supramolecular layer structure; (b) 2D supramolecular layer structures are connected into a 3D supramolecular network *via* hydrogen bonding interactions in compound 1

(Symmetry codes: iii:  $1-x, -y, 1-z$ ; iv:  $1.5-x, -0.5+y, 1.5-z$ ; v:  $x, -y, 0.5+z$ )

### 3.2 PXRD

Phase purity of the bulk material was confirmed by comparison of its PXRD patterns with the simulated pattern from the single-crystal X-ray diffraction study (Fig. S3).

### 3.3 TGA

TGA result of compound 1 is provided in the Supporting Information (Fig. S4). Experimental result indicates that 1 lost its two coordinated water molecules from 110 to 210 °C (expt. 8.56%, calcd. 9.19%). A total mass loss of 52.96% from 370 to 990 °C can be attributed to the release of  $L^{2-}$  ligand

(calcd. 53.60%).

### 3.4 Fluorescent property

Under the same situation the fluorescent properties of compound **1** and the ligand H<sub>2</sub>L have been measured in the solid state at room temperature. As shown in Fig. 4, the free ligand exhibits emission maxima at 381 nm upon 220 nm excitation, which can be attributed to the  $\pi$ - $\pi^*$  or n- $\pi^*$  intraligand electronic transitions including the -N=N- based  $\pi$ - $\pi^*$  transition<sup>[20]</sup>. Compound **1** displays the emission maxima at 384 nm when excited at 222 nm. Compound **1** displays similar emission, which can be mainly assigned to the intraligand electronic transfer.

### 3.5 Electrochemical property

We performed photoelectric conversion efficiency measurements for compound **1**. Fig. 5 shows photocurrent-photovoltaic curves of dye-sensitized solar cell (DSSC) based on compound **1**/N719/TiO<sub>2</sub> and N719/TiO<sub>2</sub> photoanodes. As shown in Fig. 5, the photovoltaic performances of DSSC based on compound **1**/N719/TiO<sub>2</sub> photoanode are improved relatively to that of DSSC based on N719/TiO<sub>2</sub> photoanode. The short-circuit photocurrent ( $J_{sc}$ ), opencircuit photovoltage ( $V_{oc}$ ), fill factor ( $FF$ ), and photoelectric conversion efficiency ( $\eta$ ) of DSSC for compound **1** and N719 co-sensitization improved from 10.58 mA·cm<sup>-2</sup>, 648 mV, 0.49, 3.45% to 11.71 mA·cm<sup>-2</sup>, 678 mV, 0.57, 4.5%, respectively. As we know, H<sub>2</sub>L is a rigid ligand including simultaneously benzene and quinoline rings. In compound **1**, each 1D zig-zag chain is connected with adjacent chains to form a 3D supramolecular network by hydrogen bonds. All of these can make compound **1** possess a relatively larger  $\pi$ -conjugated system and a highly rigid framework structure with excellent aggregation-induced emission (AIE) properties. The enhancement of photovoltaic performances of DSSC indicates that the co-sensitization of compound **1** and N719 are positive for the transfer and collection of electrons. An increasing  $J_{sc}$  is due to the increase of light harvesting in DSSC.

It is widely known that the absorption peak of N719 is 550 nm in visible light region. The combination of compound **1** and N719 enhances the absorption intensity in the 300~400 nm range of DSSC, resulting in a higher light harvesting. The increase of  $FF$  hints that the electron transfer resistance at the interface of compound **1**/N719/TiO<sub>2</sub> is lower than that for N719/TiO<sub>2</sub>. Above results imply the HOMO and LUMO levels of compound **1** matched the energy level of TiO<sub>2</sub> conduction band. In a whole, the co-sensitization of compound **1** and N719 is beneficial to  $\eta$  of DSSC by enhancing the absorption of 300~400 nm range.

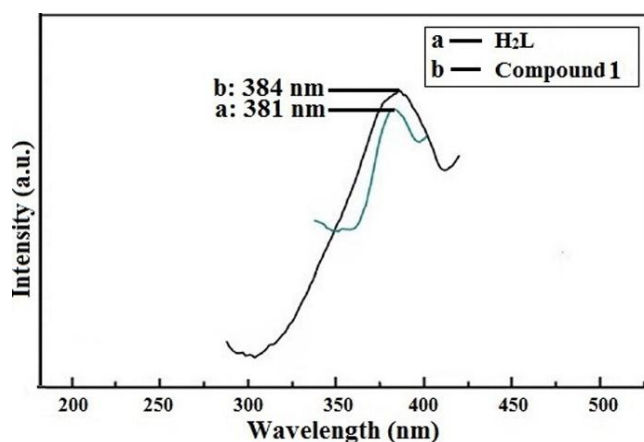


Fig. 4. Solid-state fluorescent spectrum of the H<sub>2</sub>L (a) and compound 1 (b) at room temperature

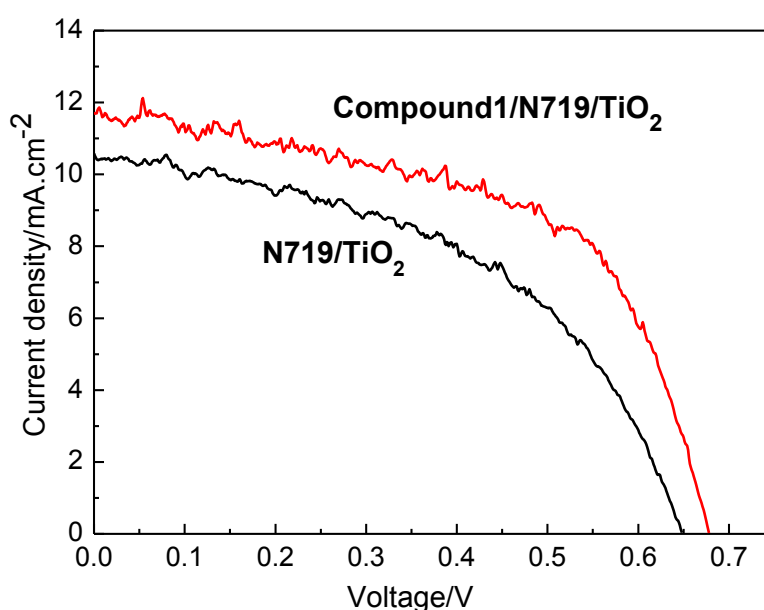


Fig. 5. Photocurrent-photovoltaic curves of dye-sensitized solar cell based on compound 1/N719/TiO<sub>2</sub> and N719/TiO<sub>2</sub> photoanodes

#### 4 CONCLUSION

In summary, a new supramolecule zinc coordination polymer has been successfully synthesized under solvothermal conditions. Compared with co-sensitization with dye N719/TiO<sub>2</sub>, photoelectric conversion efficiency has a definite increase based on compound 1/N719/TiO<sub>2</sub> photoanodes, because the modification of TiO<sub>2</sub> electrode with compound 1 and N719 not only extends the photoresponse of DSSC to the UV region of the solar spectrum, but also intensifies the optical spectrum absorption. The fluorescent properties and electrochemical properties of compound 1 demonstrate that it might provide a potential application in the region of photology and electrochemistry.

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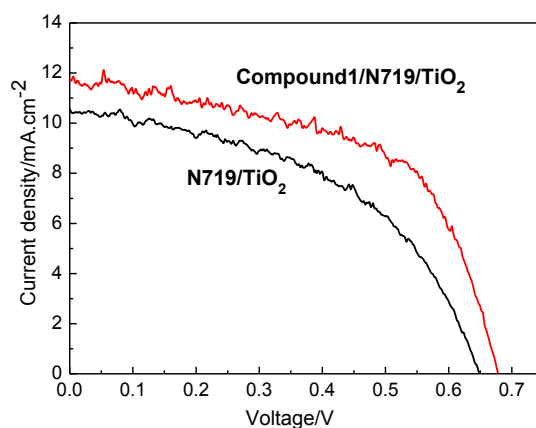
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## a 3D Supramolecular Znic Coordination Polymer

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One new 3D supramolecular Zn(II) coordination polymer based on H2L (H2L = 4-[(8-hydroxy-5-quinolynyl)azo]-benzoic acid),  $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2]_n$  (**1**), has been solvothermally synthesized. This compound displays a one-dimensional (1D) zig-zag chain structure connected into a three-dimensional (3D) supramolecular network through hydrogen bonding interactions. Compound **1** is the first example of azo coordination compound co-sensitized  $\text{TiO}_2$  photoanode with N719. The result demonstrates the compound **1**/N719/ $\text{TiO}_2$  solar cell exhibited excellent photovoltaic performance. Fluorescent properties were also performed.